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Hydrogen bonding properties and intermediate structure of *N*-(2-carboxyphenyl)salicylideneimine



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The hydrogen bonding properties, the nature of the tautomeric structure and dimerization of *N*-(2-carboxyphenyl)salicylideneimine **1** has been studied. The crystal and molecular structure of **1** has been determined by single-crystal X-ray diffraction analysis. This compound forms a dimer in the solid state, which is held together by two strong intermolecular O–H...O bridges [O(1)...O(2a) = 2.455(1) Å]. This dimeric structure is further stabilized by two intramolecular N–H...O hydrogen bonds [N(1)...O(1) = 2.654(1) and N(1)...O(2) = 2.663(1) Å]. In this way, an eight-membered pseudocycle is created. However, in methanol or acetonitrile solution, no dimerization was observed according to ¹H-NMR, IR and UV measurements. It was also found that this compound exists as an intermediate form between a phenol-imine and an *o*-quinoid structure. In addition, a derivative soluble in chloroform, 2-[2-hydroxy-5-(2-butyl)benzylideneamino]benzoic acid **3**, was examined for comparison.

Introduction

In recent years, a number of studies have been reported concerning the reversible solid-state photochromic or thermochromic reaction¹ of *N*-salicylideneaniline ('anil') compounds.² Organization of bistable organic molecules in the solid state is of great current interest in the context of molecular data storage.^{3,4} The reversible changes in colour of the anil crystals upon illumination or heating are accompanied by a transition that takes place between two tautomeric structures due to intramolecular proton transfer. These tautomers, a phenol-imine structure **I** and a quinoid structure **II** in which the proton is located at the nitrogen, are shown in Fig. 1. This behaviour of *e.g.* *N*-(2-hydroxybenzylidene)aniline and its derivatives has been extensively studied by UV, IR, X-ray diffraction, Raman and NMR spectroscopy. Various studies were carried out with these systems in order to establish the existence of intramolecular hydrogen bonding stabilizing one of the tautomeric forms.² Until now, most of the X-ray structures known for this class of compound have been referred to as phenol-imine tautomers.⁵ However, a few quinoid structures⁶ have been established as well *e.g.* *N*-salicylidene-2-hydroxyaniline (measured at 123 K)^{6b} and 2,3-dihydroxyphenylmethanimine-*α*-(2-hydroxymethyl)benzene (at 300 K).^{6d}

Schiff base compounds are often used as ligands in coordination chemistry because they are generally known for their metal binding ability, and in particular salicylaldimines are useful for the synthesis of transition metal complexes. Noteworthy examples include Cu,⁷ Fe⁸ and Mn⁹ complexes. We have synthesized *N*-(2-carboxyphenyl)salicylideneimine **1** as tridentate ligand for the formation of oxovanadium complexes,¹⁰ and

found that this compound exhibits an interesting dimeric structure in the solid state. Most intriguing is the discovery that this compound exists as an unusual intermediate form between a phenol-imine and a quinoid structure.

Results and discussion

Synthesis and X-ray analysis of **1**

Compound **1** was prepared according to a literature procedure¹¹ as described in the Experimental section. Crystals suitable for X-ray analysis were obtained from a concentrated methanolic solution of **1** by slow evaporation of the solvent. Part of the compound decomposed during crystallization due to the sensitivity of the molecule towards methanol. Crystallization from other organic solvents yielded crystals of inferior quality. The molecular structure (measured at 295 K) and the adopted atom numbering are presented in Fig. 2. Bond distances and angles are listed in Table 1.

The monoclinic *I*-centered unit cell contains eight molecules. In the crystal lattice two molecules are coupled by two strong intermolecular O–H...O bridges [O(1)...O(2a) = 2.455(1) Å (at 295 K)] resulting in the formation of dimers¹² which have a crystallographic imposed twofold axis. Weaker C–H...O interactions link them to infinite one-dimensional chains along the [100] vector (Table 2).

Another interesting feature of this structure is the presence of two intramolecular N–H...O hydrogen bonds which stabilize this dimer conformation [N(1)...O(1) = 2.654(1) and N(1)...O(2) = 2.663(1) Å]. The proton of the acid group is hydrogen-bonded to the imine-nitrogen atom forming a six-membered ring, whereas this proton is also hydrogen-bonded to the oxygen atom of the phenolic moiety. In this manner an eight-membered pseudocycle is created. Distances between hydrogen-bonded atoms are listed in Table 2. A comparable dimer formation is known for 2,3-dihydroxyphenylmethanimine-*α*-(2-hydroxymethyl)benzene, but in this case the hydrogen bonds connecting the dimers are significantly longer [A...D = 2.879(4) Å].^{6d}

When comparing bond distances with the mean values for

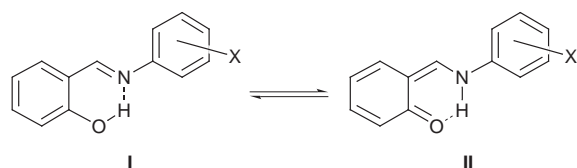


Fig. 1 Intramolecular hydrogen transfer in *N*-salicylideneaniline compounds.

similar structures referred to as phenol-imine tautomers,⁵ a number of unusual features are observed. These data were obtained from the Cambridge Structural Database (Table 3). For instance, C(6)–C(7) is considerably shortened as compared with that observed in phenol-imine structures [1.4190(16) Å instead of 1.445 Å]. C(1)–O(1) is also shortened [from 1.349 to 1.3165(15) Å], while the value of C(7)–N(1) is slightly increased [from 1.287 to 1.2999(16) Å]. The shortening of C(6)–C(7) and C(1)–O(1) bonds and the lengthening of C(7)–N(1) can be explained as follows. The hydrogen of the hydroxy group attached to C(1) is placed between atoms O(1) and O(2a) forming strong O(1)–H(1)⋯O(2a) intermolecular hydrogen bonds [O(1)–H(1) = 1.12(2); H⋯O(2) = 1.34(2) Å], thereby introducing partial tautomerization with appreciable keto character to the C(1)–O(1) bond and partial double bond character to the C(6)–C(7) bond. This causes an increase in the C(7)–N(1) bond length. However, comparing these distances with those found for quinoid structures,⁶ it is obvious that **1** cannot completely be referred to as being in the quinoid tautomeric state. For instance C(1)–O(1) and C(6)–C(7) bonds are too long [1.3165(15) instead of 1.294 Å and 1.4190(16) instead of 1.407 Å, respectively], whereas the C(7)–N(1) bond possesses too much double bond character [1.2999(16) instead of 1.327 Å]. It can be concluded that **1** exists in the solid state as an intermediate form between tautomers **I** and **II** (Fig. 4), but it could also be that the crystal contains 50% of each tautomer, providing an average structure which would be visible in unrealistic anisotropic thermal displacement parameters. To clarify this question, the crystal structure was also determined at low tem-

perature (130 K). The ORTEP plot is shown in Fig. 3. Bond distances and angles are listed in Table 1. The anisotropic thermal displacement parameters turned out not to be substantial and also the rigid body analysis¹³ is within the standard deviation. The ratio of the main axis, for example, is below 3.0 and for most atoms it is below 2.0. Bond distances of **1** recorded at 298 K are slightly shorter than those found at 130 K (Tables 1 and 2), but this was to be expected due to the thermal motion model. From these results it can be concluded that **1** is indeed an intermediate structure between phenolic and quinoid tautomers and does not exist in either two limiting structures (type **I** and **II**).

The conformation of the molecule is nearly planar. The deviation (at 295 K) of the atoms O(1), C(1)–C(10), N(1), C(13) and C(14) from the least squares plane does not exceed 0.0558(16) Å. O(2) deviates 0.6245(11) Å from the plane, whereas C(11) and C(12) lie 0.1297(19) and 0.1402(16) Å out of the plane, respectively.

Infrared spectroscopy

The infrared spectrum of **1** shows an absorption at 1691 cm^{−1}, which is attributed to a C=O stretching vibration.¹⁴ A broad O–H stretching vibration is observed at about 3450 cm^{−1}. This is indicative of hydrogen bonding, because the normal absorption band for free O–H is in the range of 3730–3520 cm^{−1}.¹⁴ A strong C=N stretching vibration band is observed at 1618 cm^{−1}. It is known that when the nitrogen atom of the C=N bond is substituted in such a way that it is able to take on a more polar character, the absorption can be found in the region 1659–1510 cm^{−1} (normal C=N is expected in the range of 1680–1650 cm^{−1}).¹⁴ In this case the hydrogen atom of the acid functionality

Table 1 Selected bond distances (Å) and angles (°) of **1** with estimated standard deviation (esd's) in parentheses measured at 130 K and 295 K, respectively

O(1)–C(1)	1.3192(16)	1.3165(15)
O(2)–C(14)	1.2809(17)	1.2744(16)
O(3)–C(14)	1.2296(18)	1.2229(18)
N(1)–C(7)	1.3022(18)	1.2999(16)
N(1)–C(8)	1.4264(16)	1.4250(15)
C(1)–C(2)	1.4070(19)	1.4050(18)
C(1)–C(6)	1.4198(19)	1.4183(17)
C(2)–C(3)	1.375(2)	1.372(2)
C(3)–C(4)	1.399(2)	1.391(2)
C(4)–C(5)	1.3725(19)	1.363(2)
C(5)–C(6)	1.414(2)	1.4102(18)
C(6)–C(7)	1.4250(19)	1.4190(16)
C(8)–C(9)	1.3923(19)	1.3917(18)
C(8)–C(13)	1.4004(19)	1.3970(17)
C(9)–C(10)	1.3808(19)	1.376(2)
C(10)–C(11)	1.384(2)	1.369(2)
C(11)–C(12)	1.383(2)	1.381(2)
C(12)–C(13)	1.3896(19)	1.3847(18)
C(13)–C(14)	1.5150(19)	1.5117(17)
C(7)–N(1)–C(8)	125.99(12)	126.07(10)
O(1)–C(1)–C(6)	118.57(12)	118.65(10)
C(1)–C(6)–C(7)	122.88(12)	122.82(11)
N(1)–C(8)–C(13)	118.47(11)	118.66(10)
C(8)–C(13)–C(14)	123.21(12)	123.32(10)
O(2)–C(14)–O(3)	126.01(13)	125.81(12)
O(2)–C(14)–C(13)	114.75(11)	114.84(11)
C(3)–C(14)–C(13)	119.23(12)	119.34(11)
C(8)–C(13)–C(14)–O(2)	−31.70(19)	−30.90(18)

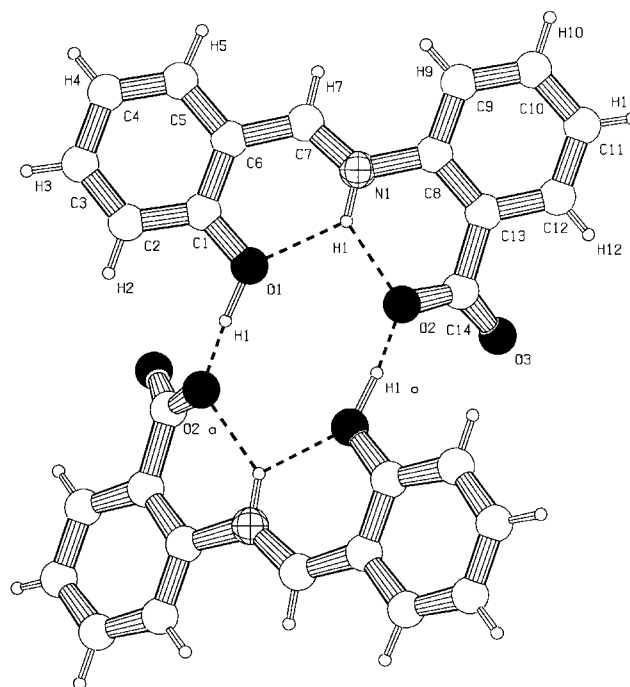


Fig. 2 A PLUTON representation of the structure of **1** measured at 295 K.

Table 2 Hydrogen bonds observed for **1** measured at 130 K and 295 K, respectively

D–H⋯A/Å	D–A/Å	D–H/Å	H⋯A/Å	D–H⋯A/°
O(1)–H(1)⋯O(2a)	2.453(1); 2.455(1)	1.10(2); 1.12(2)	1.36(2); 1.34(2)	173(2); 173(2)
N(1)–H(1')⋯O(1)	2.656(2); 2.654(1)	0.95(2); 0.97(2)	1.94(2); 1.96(2)	131(2); 126(1)
N(1)–H(1')⋯O(2)	2.667(2); 2.663(1)	0.95(2); 0.97(2)	1.95(2); 1.90(2)	131(2); 133(1)
C(7)–H(7)⋯O(3)	3.232(2); 3.253(2)	1.00(2); 0.97(1)	2.26(2); 2.30(2)	166(1); 166(1)
C(9)–H(9)⋯O(3)	3.237(2); 3.246(2)	0.93(2); 0.93(2)	2.39(2); 2.42(2)	148(2); 148(2)

Table 3 Bond distances (at 295 K) of **1** (Å) with esd's in parentheses compared with mean distances (determined at various temperatures) for related quinoid^{5a-d} and phenolic^{4a-f} structures (Å). Minimum and maximum values are given in parentheses

Bond	Distances for 1	Quinone	Phenol
C(7)–N(1)	1.2999(16)	1.327 (1.302; 1.347)	1.287 (1.266; 1.317)
C(1)–O(1)	1.3165(15)	1.294 (1.279; 1.301)	1.349 (1.323; 1.399)
N(1)–H(1')	0.97(2)	1.053 (0.903; 1.204)	1.818 (1.388; 3.536)
O(1)–H(1)	1.12(2)	1.644 (1.414; 1.836)	0.970 (0.789; 1.250)
C(6)–C(7)	1.4190(16)	1.407 (1.399; 1.413)	1.445 (1.426; 1.457)

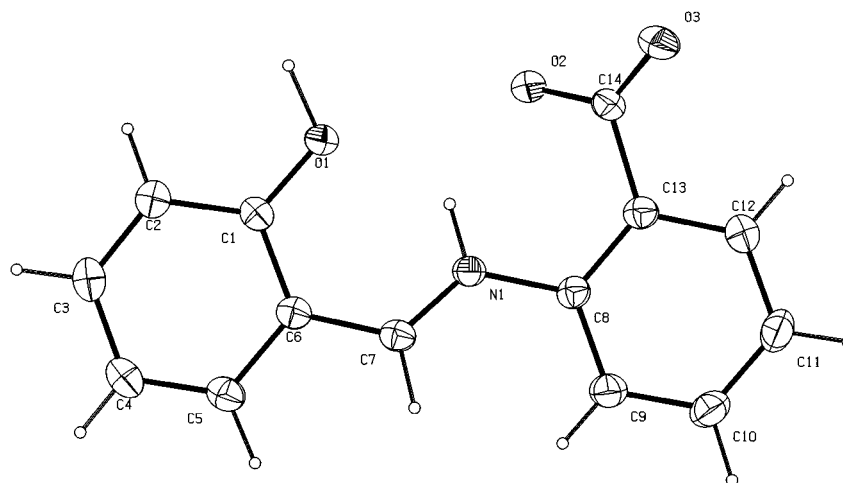


Fig. 3 An ORTEP plot of **1** measured at 130 K (50% probability level).

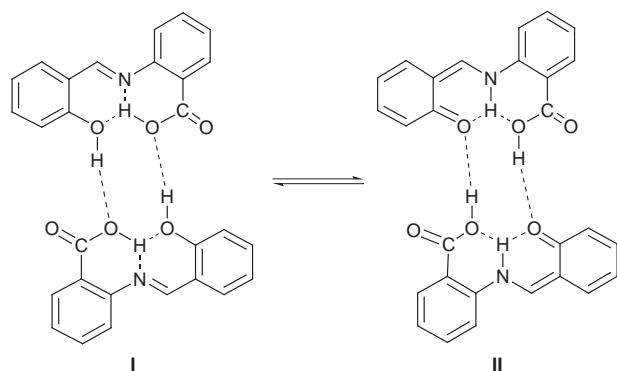


Fig. 4 Schematic representation of phenol-imine and quinoid tautomeric structures of **1**.

located on the nitrogen causes this shift. An absorption band at 1582 cm^{-1} may be assigned to a C=C stretching vibration.¹⁴

The IR spectra of solid samples and solutions are clearly different. Although in acetonitrile the absorption of the C=N bond is observed at 1620 cm^{-1} (1618 cm^{-1} for the solid sample), a shift is observed for the C=O stretching vibration from 1691 to 1727 cm^{-1} . Varying the concentration of **1** does not influence the spectrum. This indicates the absence of intermolecular hydrogen bonds. It seems that in solution the hydrogen of the acid moiety is still hydrogen bonded to the imine nitrogen, but hydrogen bonding to the phenol functionality of a second monomer does not occur. We conclude that whilst the solid-state structure shows a dimeric entity, in solution it appears to be monomeric. However, the degree and nature of dimerization in solution is very often a sensitive function of the donor and acceptor properties and the dryness of the solvent. Therefore, the difference was further corroborated by $^1\text{H-NMR}$ analysis.

$^1\text{H-NMR}$ analysis

To further support the occurrence of monomeric species of compound **1** in solution, we have carried out additional NMR analyses. $^1\text{H-NMR}$ spectra of aggregates in a hydrogen-

bonding solvent such as d^6 -dimethyl sulfoxide in general only show fully dissociated components.¹⁵ A typical $^1\text{H-NMR}$ spectrum of monomeric **1** in DMSO is shown in Fig. 5. The spectrum of **1** in acetonitrile- d^3 is similar to the spectrum recorded in DMSO, which indicates the existence of a monomeric phenol-imine tautomeric form in acetonitrile. These observations are in agreement with the IR spectra (*vide supra*).

$^1\text{H-NMR}$ spectra of **1** in methanol- d^4 were much more difficult to interpret because the ligand is not stable in methanol solution. Most likely, the molecule is attacked by methanol at the imine N(1)–C(7) bond, forming eventually, among other products, an acetal from salicylaldehyde [5.56 ppm (s, acetal proton)], 2-aminobenzoic acid [6.73–6.64 (m, 2H)] and salicylaldehyde [9.86 ppm (s, CHO)]. Although full analysis of these spectra was impossible, dimer formation does not occur under the conditions employed, because no concentration dependent shifts were observed.¹⁶

Electron spray mass measurements

Additional experiments were performed using electron spray mass spectrometry (ESMS).¹⁷ Varying the concentration of **1** in methanol starting from 1×10^{-6} to $1 \times 10^{-3}\text{ M}$ reveals a continuing increase of a mass peak of 483, which corresponds to $(2M + \text{H})$. These results differ from the observations with $^1\text{H-NMR}$ in methanol (*vide supra*). However it is known with ESMS, that it is difficult to distinguish between dimers in solution and cluster formation inside the mass spectrometer.¹⁸ Samples measured at higher concentrations (10^{-5} M and above) can give association of two molecules held together by a H^+ or a Na^+ . A lot of degradation products were also found, which is in agreement with the NMR studies. When acetonitrile is used as a solvent, no significant dimer formation was observed at the same concentrations, which was compatible with the NMR data as well. The mass spectra and NMR experiments both showed greater stability of **1** in acetonitrile than in methanol.

UV spectroscopy

The UV spectrum of **1** recorded in acetonitrile exhibits four bands at 214, 274, 336 and 429 nm. The band at 214 nm

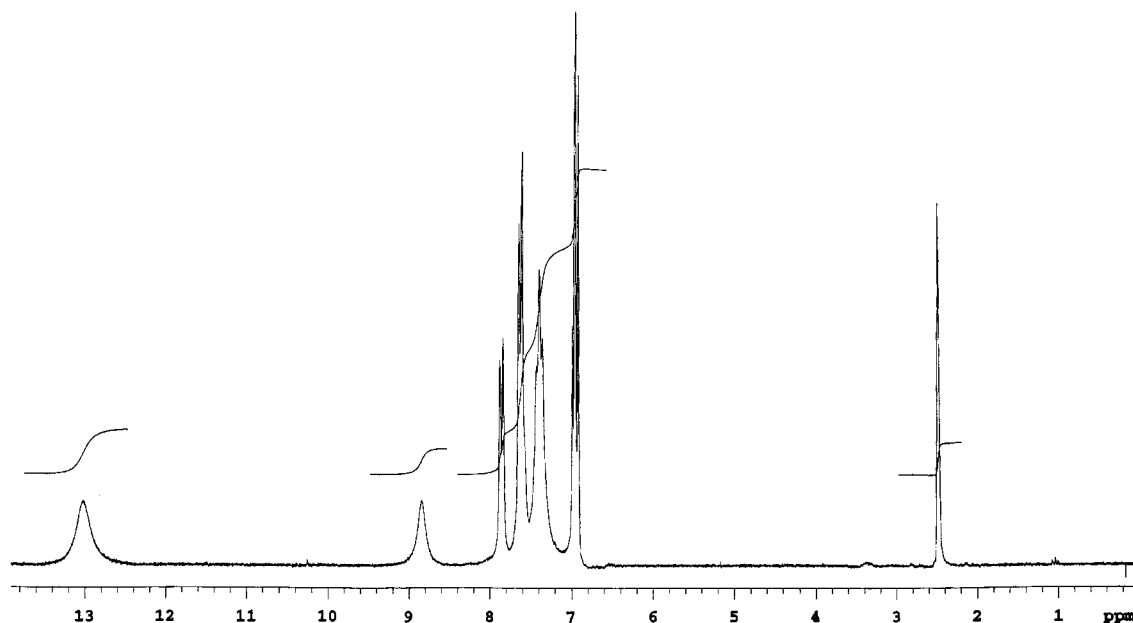


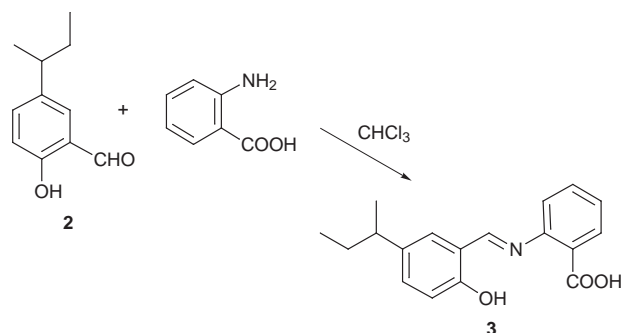
Fig. 5 ^1H -NMR spectrum of **1** in acetonitrile- d_3 .

($\epsilon = 26.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) is considered to arise from electronic $\pi\text{--}\pi^*$ transitions in the aromatic rings.^{6d} The band at 274 nm (10.6) can be assigned to $\pi\text{--}\pi^*$ transitions involving one aromatic ring and the imine functionality. The band at even longer wavelength, 336 nm (9.5), probably arises from an intramolecular charge transfer interaction. Strong intramolecular hydrogen bonding between the carboxylic hydrogen and the imino-nitrogen forces planarity, which facilitates charge transfer.¹⁹ The band at 429 nm (0.3) is assigned to a $\text{n--}\pi^*$ transition confirming that **1** possesses partial *o*-quinoid character.²⁰

Synthesis and structural analysis of related salicylideneimine **3**

To further study the ability of these compounds to form hydrogen-bonded aggregates in solution, the alkyl-substituted derivative **3** was synthesized which shows higher solubility in chloroform. In this solvent, salicylideneimine **1** is insoluble. If dimerization was possible in solution with this type of compound, we expected it to occur in this solvent.¹⁵

2-[2-Hydroxy-5-(2-butyl)benzylideneamino]benzoic acid **3** was synthesized by the Schiff-base formation of 2-hydroxy-5-(2-butyl)benzaldehyde **2** and 2-aminobenzoic acid in chloroform (Scheme 1). Compound **2** had been synthesized previously



Scheme 1 Synthesis of **3**.

via a Reimer–Tiemann reaction,²¹ but the yield was rather low (30%). Therefore we developed a route analogous to the literature²² procedure in which *o*-hydroxyaryl aldehydes are formed by treating aryloxymagnesium bromides with paraformaldehyde in the presence of triethylamine. In this way, **2** was obtained in 63% yield.

Electron spray mass spectrometry (ESMS) was again used to

examine possible dimer formation of **3**. In chloroform, a significant amount of a dimer with a mass of 595 ($2M + \text{H}$) was observed besides the mass peak of the monomer (298 corresponds to $M + \text{H}$). Molecular weight determinations in chloroform at 38 °C of 0.015, 0.04, 0.07 and 0.09 M solutions, however, indicated that dimerization does not occur. Also concentration dependent ^1H -NMR measurements in deuterated chloroform are consistent with a monomeric phenol-imine tautomeric structure. Again, cluster formation seems to occur inside the mass spectrometer. Results of experiments in acetonitrile show comparable results as discussed earlier for imine **1** *i.e.* neither ESMS nor ^1H -NMR gave any evidence for dimerization. Also Schiff base **3** is not stable in methanol solution. In the mass spectra as well as in the ^1H -NMR spectra, several degradation products are observed.

The UV spectrum recorded in chloroform resembles that of **1** recorded in acetonitrile. Also in this case four bands are observed, at 242 ($\epsilon = 18.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), 279 (11.1), 312 (9.4) and 438 nm (1.4). The latter shows that **3** also possesses partial *o*-quinoid character as was observed for **1**.

The infrared spectra of **3** in the solid state as well as in solution are very similar to those of **1**. The absorptions in the solid state are at 1693 (C=O), 1622 (C=N), 1568 (C=C) and at around 3450 cm^{-1} a broad O–H band is observed. In chloroform solution the C=O stretching vibration band shifts towards 1727 cm^{-1} and the C=N stretching vibration band is located at 1627 cm^{-1} .

Conclusions

A dimeric structure was obtained for **1** in the solid state with short intermolecular hydrogen bonds giving rise to the formation of an eight-membered pseudocycle. Variable temperature X-ray analyses show that its structure can be described best as intermediate between phenol-imine and quinoid tautomeric forms and is not an average of the two limiting structures. We have shown using ^1H -NMR, UV and IR measurements, that in solution the compound exists as a monomer. In addition a related salicylideneimine **3**, soluble in chloroform, was investigated. This Schiff base showed similar properties to that of **1**. Compound **3** most probably exists as a dimer in the solid state as well as, for instance, IR spectra of solid samples and of solution samples are very similar in the O–H region as well as in the carbonyl and imine region, which indicates similar dimerization behaviour for both compounds.

Experimental

Proton and carbon-13 NMR spectra were recorded on a Varian VXR-300 spectrometer (at 300 MHz and 75.4 MHz, respectively). Chemical shifts are reported in δ units (ppm) relative to the residual deuterated solvent signals. All solvents used for NMR experiments were dried on molecular sieves (4 Å), degassed and stored under an atmosphere of argon. High-resolution mass spectra were obtained on an AEI MS-902 spectrometer by electron impact (EI), electron spray (ES) mass spectra on a NERMAG mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 841 spectrometer. UV-VIS spectra were recorded on a HP-8453 spectrophotometer. Elemental analyses were performed in the Microanalytical Department of our laboratory.

N-(2-Carboxyphenyl)salicylideneimine (1)

To a hot solution of *o*-aminophenol (3.43 g, 0.025 mol) in absolute ethanol (15 ml) was added a solution of salicylaldehyde (3.05 g, 0.025 mol) in absolute ethanol (5 ml). The orange reaction mixture was heated for 5 min and then cooled in an ice bath. Filtration of the orange precipitate yielded **1** (5.47 g, 90%). Crystals suitable for X-ray analysis were obtained from a concentrated solution of **1** in methanol by slow evaporation of the solvent (yield 20–40%) (Found: C, 69.63; H, 4.75; N, 5.70. $C_{14}H_{11}NO_3$ requires C, 69.70; H, 4.60; N, 5.81%); δ_H (300 MHz, DMSO- d_6) 13.00 (br, 2H, H1 + H1'), 8.83 (br, 1H, H7), 7.84 (d, 1H, $J = 6.96$ Hz, H12), 7.62–7.60 (m, 2H, H11 + H5), 7.45–7.30 (m, 3H, H10 + H9 + H3), 6.96–6.91 (m, 2H, H2 + H4); δ_H (300 MHz, CD_3CN) 8.70 (br, 1H, H7), 7.94 (d, 1H, $J = 7.69$ Hz, H12), 7.65–7.58 (m, 1H, H11), 7.55–7.52 (m, 1H, H5), 7.40–7.33 (m, 3H, H10 + H9 + H3), 6.98–6.93 (m, 2H, H2 + H4); ESMS (CH_3CN) m/z 242 (M + H); ESMS (MeOH) m/z 242 (M + H), 264 (M + Na), 301, 360, 483 (2M + H), 585 (2M + Na) (HRMS calcd. for $C_{14}H_{11}NO_3$: 241.074. Found: 241.074); $\lambda_{max}(CH_3CN)/nm$ 214 (ϵ 10^3 M $^{-1}$ cm $^{-1}$ 26.1), 274 (10.6), 336 (9.5), 429 (0.3).

2-Hydroxy-5-(2-butyl)benzaldehyde (2)

Compound **2** was obtained analogously to a literature procedure:²² yield after Kugelrohr distillation (97 °C at 0.4 mmHg) as a slightly yellow oil, 63%. δ_H (300 MHz, $CDCl_3$) 10.86 (s, 1H, CHO), 9.87 (s, 1H, OH), 7.38–7.33 (m, 2H), 6.92 (d, 1H, $J = 8.05$ Hz), 2.60 (heptet, 1H, $J = 7.0$ Hz, CH), 1.65–1.50 (m, 2H, CH_2), 1.23 (d, 3H, $J = 6.83$ Hz, CH_3), 0.81 (t, 3H, $J = 7.45$ Hz, CH_3); δ_C (75.4 MHz, $CDCl_3$) 196.6 (CHO), 159.6 (C), 138.9 (C), 135.9 (CH), 131.4 (CH), 120.2 (C), 117.2 (CH), 40.4 (CH), 30.9 (CH_2), 21.5 (CH_3), 11.9 (CH_3) (HRMS calcd. for $C_{11}H_{14}O_2$: 178.099. Found: 178.100).

2-[2-Hydroxy-5-(2-butyl)benzylideneamino]benzoic acid (3)

To a solution of 5-*sec*-butylsalicylaldehyde (0.200 g, 1.12 mmol) in chloroform (10 ml) was added 2-aminobenzoic acid (0.155 g, 1.12 mmol) in chloroform (10 ml). The reaction mixture was stirred for 2 h. Sodium sulfate was added and the yellow solution was stirred for an additional 30 min. After filtration and slow evaporation **3** was obtained as a yellow powder (0.24 g, 72%) (Found: C, 72.19; H, 6.35; N, 4.68. $C_{14}H_{11}NO_3$ requires C, 72.71; H, 6.44; N, 4.71%); δ_H (300 MHz, $CDCl_3$) 11.15 (br, 2H, H1 + H1'), 8.44 (s, 1H, H7); 8.07 (d, 1H, $J = 7.88$ Hz, H12), 7.54–7.49 (m, 1H, H11), 7.27 (t, 1H, $J = 7.69$ Hz, H5), 7.17–7.11 (m, 3H, H10 + H9 + H3), 6.98 (d, 1H, $J = 8.42$ Hz, H2), 2.51–2.44 (m, 1H, CH); 1.53–1.43 (m, 2H, CH_2), 1.13 (d, 3H, $J = 6.59$ Hz, CH_3), 0.73 (t, 3H, $J = 7.33$ Hz, CH_3); ESMS ($CHCl_3$) m/z 298 (M + H) and 595 (2M + H); ESMS (CH_3CN) m/z 298 (M + H); ESMS (MeOH) m/z 138 (*o*-aminophenol + H), 178 (5-*sec*-butylsalicylaldehyde + H), 193, 247, 298 (M + H), 595 (2M + H) (HRMS calcd. for

$C_{18}H_{19}NO_3$: 297.136. Found: 297.139); $\lambda_{max}(CHCl_3)/nm$ 242 (ϵ 10^3 M $^{-1}$ cm $^{-1}$ 18.7), 279 (11.1), 312 (9.4), 438 (1.4).

X-Ray crystal structure determination of 1

An orange-red coloured block-shaped crystal of **1** having approximate dimensions of 0.15 × 0.15 × 0.40 mm mounted on top of a glass fiber was used for the X-ray study.

Crystal data. $C_{14}H_{11}NO_3$, $M = 241.25$, monoclinic, space group $I2/a$, $T = 295$ K, $a = 14.840(1)$, $b = 6.813(1)$, $c = 22.680(1)$ Å, $\beta = 97.796(6)^\circ$, $V = 2271.9(4)$ Å 3 , $Z = 8$, $D_x = 1.411$ g cm $^{-3}$, $\mu(Mo-K\alpha) = 1.0$ cm $^{-1}$, $F(000) = 1008$; $T = 130$ K, $a = 14.831(1)$, $b = 6.718(1)$, $c = 22.660(5)$ Å, $\beta = 97.61(1)^\circ$, $V = 2237.8(6)$ Å 3 , $Z = 8$, $D_x = 1.432$ g cm $^{-3}$, $\mu(Mo-K\alpha) = 1.0$ cm $^{-1}$, $F(000) = 1008$.

Data collection, structure analysis and refinement. The intensity data were collected on an Enraf-Nonius CAD-4F diffractometer with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) using $\omega/2\theta$ mode with ω scan width = $0.85 + 0.34 \tan \theta$ at 295 K and $0.80 + 0.34 \tan \theta$ at 130 K, respectively. Intensity data were corrected for Lorentz and polarization effects, scale variation, but not for absorption and were reduced to F_o^2 . The structure was solved by direct methods with SHELXS86.²³ Refinement on F^2 was carried out by full-matrix least-squares techniques: observance criterion $F^2 \geq 0$ was applied during refinement. A subsequent difference Fourier analysis resulted in the location of all the hydrogen atoms, which coordinates and isotropic thermal displacement parameters were refined. The crystal (at 295 K) exhibited some secondary extinction for which the F_c values were corrected by refinement of an empirical isotropic extinction parameter. Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $wR(F^2) = 0.1148$ for 2364 reflections with $F_o^2 \geq 0$ and $R(F) = 0.0388$ for 1967 reflections obeying $F_o \geq 4.0 \sigma(F_o)$ criterion and 208 parameters. A final difference Fourier map did not show residual peaks outside the range $\pm 0.22(4)$ e Å $^{-3}$. Final refinement on F^2 (at 130 K) converged at $wR(F^2) = 0.1001$ for 2192 reflections with $F_o^2 \geq 0$ and $R(F) = 0.0359$ for 1783 reflections obeying $F_o \geq 4.0 \sigma(F_o)$ criterion and 207 parameters. A final difference Fourier map did not show residual peaks outside the range $\pm 0.21(5)$ e Å $^{-3}$.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme see 'Instructions for Authors (1998)', *J. Chem. Soc., Perkin Trans. 2*, available via the RSC Web page (<http://www.rsc.org/authors>). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/159. See: <http://www.rsc.org/suppdata/p2/1999/807/> for crystallographic files in .cif format.

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